

EVALUATION OF FINE-PARTICLE SIZE CATALYSTS USING BITUMINOUS AND SUBBITUMINOUS COALS

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ABSTRACT

The objectives of Sandia's fine-particle size catalyst testing project are to evaluate and compare the activities of fine-particle size catalysts being developed in DOE/PETC's Advanced Research Coal Liquefaction Program by using Sandia's standard coal liquefaction test procedures. The first test procedure uses bituminous coal (DECS-17 Blind Canyon coal), phenanthrene as the reaction solvent, and a factorial experimental design that is used to evaluate catalysts over ranges of temperature, time, and catalyst loading. The best catalyst evaluated to date is West Virginia University's iron catalyst that was impregnated onto the coal. Current work is aimed at developing a standard test procedure using subbituminous Wyodak coal. This test is being developed using Pacific Northwest Laboratories' 6-line ferrihydrite catalyst and coal samples impregnated with either molybdenum or iron at Argonne National Laboratories. Results of testing catalysts with bituminous coal will be summarized and the development of the subbituminous coal test procedure will be presented.

INTRODUCTION

There are several potential advantages of using cheap, unsupported, fine-particle size (<40 nm) catalysts in direct coal liquefaction. Among these are improved coal/catalyst contact due to good dispersion⁽¹⁾ of the catalyst, and the potential for using low quantities of catalyst ($<0.5\%$ based on the weight of coal) because of their very high surface areas. These catalysts could be combined with the coal as either active catalysts or catalyst precursors that would be activated in situ. Research efforts to develop fine-particle size, unsupported catalysts for direct coal liquefaction^(2,3) indicate that the use of these catalysts could result in significant process improvements, such as enhanced yields of desired products, less usage of supported catalyst, and possibly lower reaction severities. Realization of these improvements would result in decreased costs for coal liquefaction products.

The goal of Sandia's project is to evaluate and compare the activities/selectivities of fine-particle size catalysts being developed in the DOE/PETC Advanced Research (AR) Liquefaction Program by using standard coal liquefaction activity test procedures. Since bituminous and subbituminous coals have significantly different properties, it is feasible that catalysts may perform differently with these coal types. Because all previous testing has been done with the DECS-17 Blind Canyon bituminous coal, it is important to develop the capability of evaluating catalysts using a subbituminous coal. Wyodak coal from the Argonne Premium Coal Sample Program⁽⁴⁾ was chosen for development of this test primarily because there has been significant research work done with Argonne's premium coals and because using existing well characterized samples eliminates the need to collect, prepare, and characterize another coal. The purpose of the current work is to develop a test using the Wyodak subbituminous coal.

EXPERIMENTAL SECTION

Materials. Two coals are being used in this project. DECS-17 Blind Canyon bituminous coal was obtained from The Penn State Coal Sample Bank⁽⁵⁾. It's a high volatile A bituminous coal with 3.74% moisture, 0.36% iron, 0.02% pyritic sulfur, and 7.34% mineral matter (on a dry basis). The particle size is -60 mesh. Subbituminous Wyodak coal was obtained from the Argonne Premium Coal Sample Program. It has 28.09% moisture, 0.17% dry pyritic sulfur, and 9.82% mineral matter (on a dry basis using the Parr formula). Phenanthrene is used as the reaction solvent. Elemental sulfur was added to the reactors to sulfide catalyst precursors.

Microautoclave Reactors. Testing is performed using batch microautoclaves made of type 316 stainless steel components. The total volume of a reactor is 43 cm^3 with a liquid capacity of 8 cm^3 . The reactors are loaded with 1.67g coal and 3.34g phenanthrene. If the reaction is catalytic, the catalyst loading is either 0.5 wt% or 1.0 wt% of the amount of coal loaded into the reactor. The amount of sulfur addition (if needed) is specified by the catalyst developer. Reactors are charged to 800 psig H_2 (cold charge) and heated to reaction temperatures in fluidized-sand baths. Temperatures, pressures and times are recorded with a digital data acquisition system every 30 seconds during the course of the reactions. Following the heating period, the reactors are rapidly cooled to ambient temperature in a water bath and a gas sample is collected. The reaction data is analyzed to determine the actual reaction time and the averages and standard deviations for reaction temperature and pressure. Heat-up times and cooling times are also determined.

Product Workup Procedures. The reaction products are rinsed out of the reactors with tetrahydrofuran (THF). THF and heptane solvent solubilities are measured using a Millipore 142 mm diameter pressure filtration device with air pressurization and Duopore (0.45 micron) filter paper. The filter cakes are rinsed twice with THF or heptane as appropriate. After the filtrations are complete, the filter papers are dried under vacuum at 70°C, cooled to room temperature, and weighed to determine the insoluble portions. The THF soluble material is quantitatively sampled for gas chromatographic (GC) analysis, which is used to determine the reaction solvent recovery and final composition. THF is removed from the solubles by rotary evaporation prior to determining heptane conversion. The quantity of gases (CO, CO₂, CH₄, C₂H₆) produced in a reaction is calculated using the post-reaction vessel temperature and pressure with the ideal gas law and the mole percents in the gas sample as determined using a Carle GC and standard gas mixtures.

Factorial Experimental Design and Analysis. The factorial experimental design (Figure 1) evaluates the effects of three variables at two levels: temperature (350 and 400°C), time (20 and 60 minutes), and catalyst loading of either 0.0 wt% or 1.0 wt% of the amount of coal loaded into the reactor. With this full factorial experimental design, the experimental results are evaluated for all combinations of levels of the three variables so that 2³ evaluations are required. Additional reactions are performed at the center point of this cubic design. An Analysis of Variance (ANOVA) is performed to estimate the effects of the experimental variables and to statistically test their significance. Replication of the experiments is used to estimate measurement error and to reduce its effect on the estimated effects of the variables. Models are constructed using the estimates of the effects of the variables to calculate the expected experimental results for specified sets of reaction conditions⁽⁶⁾. The controlled factors used in the ANOVA are the measured average reaction temperature, measured reaction time, and the actual weight of catalyst used.

Catalyst. The catalyst chosen for development of the subbituminous coal test was a 6-line ferrihydrite catalyst precursor supplied by J. Linehan of Pacific Northwest National Laboratories (PNNL). This catalyst had been evaluated previously using Sandia's standard test procedure with Blind Canyon coal. It was the best catalyst in the form of a powder found to date. No pretreatment is required. Testing of this material used a 1:1 sulfur to catalyst precursor ratio on a weight basis. All reactions including thermal reactions had the same amount of added sulfur.

RESULTS AND DISCUSSION

Procedure for Comparing the Wyodak Coal with the DECS-17 Blind Canyon Coal

Testing of fine-particle size catalysts at Sandia has been based on a test using DECS-17 Blind Canyon coal, a bituminous coal. Since bituminous and subbituminous coals have significantly different properties, it is feasible that some catalysts may perform better with one coal type than with the other coal type. Therefore, it is important to have the capability of evaluating catalysts using a subbituminous coal. Wyodak coal from the Argonne Premium Coal Sample Program was chosen for development of this test primarily because there has been significant research work done with Argonne's premium coals and because using available samples eliminates the need to collect, prepare and store another coal.

One aspect of developing a test with Wyodak coal entails determining how results will be compared to those obtained with Blind Canyon coal. To do this comparison, we decided to evaluate Wyodak coal with PNL's 6-line ferrihydrite catalyst that had been evaluated previously at Sandia using the Blind Canyon coal. This is the best catalyst in the form of a powder evaluated to date at Sandia. The same factorial experimental design that is being used in the Blind Canyon coal test will be used with Wyodak coal. This decision was made because it was felt that the ranges of the three variables were broad enough to also apply to the Wyodak coal. One of the many significant differences between Blind Canyon coal and Wyodak coal is the moisture content: Blind Canyon coal has 3.74% water and Wyodak has 28.09% water. To ensure that good comparisons could be made, the Wyodak coal was dried to about 6% water. This amount was chosen because it was close to the value for Blind Canyon coal and was also close to the water contents of several coal samples that had been impregnated with either Mo or Fe by Karl Vorres at Argonne National Laboratory. The Fe impregnated sample had 6.79% water and the Mo impregnated sample had 6.19% water. These impregnated coals will be evaluated after the subbituminous coal test is finalized. The dry sulfur contents of the Wyodak coal and the DECS-17 Blind Canyon coal are 0.63% and 0.44% respectively. The dry mineral matter is 10.01% for Wyodak coal (based on the modified Parr formula) and 7.49% for the DECS-17 coal.

Experimental Test Procedure

The testing used 1.67g Wyodak coal, 3.34g phenanthrene, and 1 wt % sulfur for all reactions. Catalyst loadings were either 0%, 0.5%, or 1.0 wt % based on the experimental design. Sulfur was added to all reactions because previous studies with Blind Canyon coal showed that Fe in the mineral ankerite was converted to pyrrhotite during reaction thus yielding a catalytic effect. The impact of sulfur addition on Wyodak coal conversion will be quantified by comparing results to reactions of Wyodak coal without sulfur addition. Figure 1 shows the factorial experimental design used in the testing.

Testing Results for PNL's 6-Line Ferrihydrite Catalyst with Wyodak Coal

Results for THF conversion (%), heptane conversion (%), 9,10-dihydrophenanthrene (DHP (%)) in the reaction product, and gas yield (mol%) from this testing are shown in Figures 2-5. The values in

parentheses for each reaction condition are the average measured values obtained using PNL's catalyst with the Blind Canyon coal. The following discussion is based on these measured results. A statistical analysis of this data is currently being performed and will include a comparison of the Blind Canyon coal results and the Wyodak coal results.

Results for THF conversion (Figure 2) suggest that at low severity conditions (350°C, no catalyst), THF conversions are about 7.5% (absolute) lower for Blind Canyon coal. However, for all other conditions THF conversions are higher for Blind Canyon coal. At the most severe reaction condition (400°C, 60 minutes, 1% catalyst), Blind Canyon coal yielded 89.6 % conversion whereas Wyodak coal gave about 75.5%.

Results for heptane conversion (Figure 3) suggest that Wyodak coal may give higher heptane conversions for most if not all reaction conditions. Results at the lowest severity condition (350°C, 20 minutes, 0% catalyst) show a small negative conversion (-3.0%) for Blind Canyon coal, but an average conversion of 9.9% was obtained for Wyodak coal. Results at the highest severity condition (400°C, 60 minutes, 1% catalyst), gave an average 34.3% conversion for Wyodak coal but only 26.8% for Blind Canyon coal. Results at 400°C without catalyst show some overlap of results from the two coals. The statistical analysis will determine what differences are statistically significant.

Figure 4 shows the weight % of DHP (based on GC analyses of phenanthrene and DHP in the reaction product) after completion of the run. Results suggest that the Blind Canyon coal yields more DHP at all reaction conditions. At 400°C, 60 minutes, 1% catalyst, there is almost double the amount of DHP in the reaction product with Blind Canyon coal. The lower DHP in the product of the Wyodak reactions may be due to several causes. One possibility is that some of the hydrogen in the DHP is transferred to additional light reaction products as evidenced by higher heptane conversions with Wyodak coal. This could be due to Wyodak's lower coal rank. Another possibility is that Blind Canyon coal may yield higher DHP because some of the ankerite in the coal may get converted to pyrrhotite during the reaction and thus yield extra hydrogenation catalyst.

Figure 5 shows the total amount of gases (CO, CO₂, CH₄, C₂H₄) produced at each reaction condition. Results suggest that there are significantly more gases present with the Wyodak coal. For Blind Canyon coal, the total amount of gases ranges from about 0.30 to 1.86 mol% whereas for Wyodak coal the total amount ranges from about 1.90 to 4.35 mol%. In all cases, CO₂ is by far the biggest contributor to the gas yield, which was also observed with Blind Canyon coal.

CONCLUSIONS

Initial efforts towards developing a subbituminous coal test are aimed at comparing the reactivities of the Wyodak subbituminous coal and the Blind Canyon bituminous coal. Therefore, the same factorial experimental design was used with the Wyodak coal as was used previously with the Blind Canyon coal. In addition, PNL's 6-line ferrihydrite catalyst precursor was used in the development of the Wyodak coal test procedure because this catalyst is the best powder catalyst found to date in Sandia's tests with Blind Canyon coal. Results show that Blind Canyon coal yields higher DHP amounts in the reaction products and higher tetrahydrofuran (THF) conversions at the higher severity conditions. Wyodak coal gives higher heptane conversions and higher gas yields for all conditions tested.

FUTURE WORK

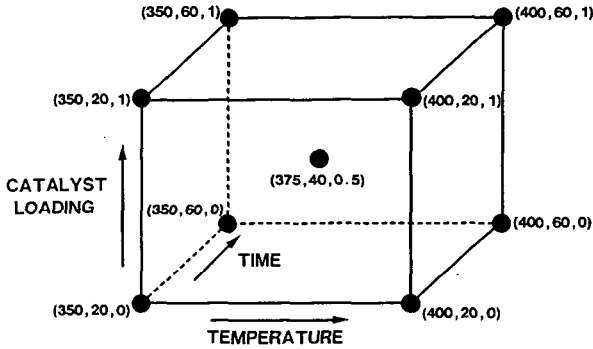
Future work on developing the catalyst test with Wyodak coal will include performing the statistical analyses of the results obtained from the experiments with PNL's 6-line ferrihydrite catalyst. Results from this study with Wyodak coal will be statistically compared to previous results obtained from Blind Canyon coal with PNL's catalyst.

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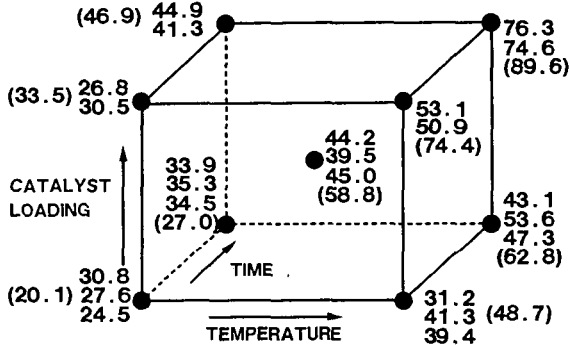
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FIGURE 1.
FACTORIAL EXPERIMENTAL DESIGN



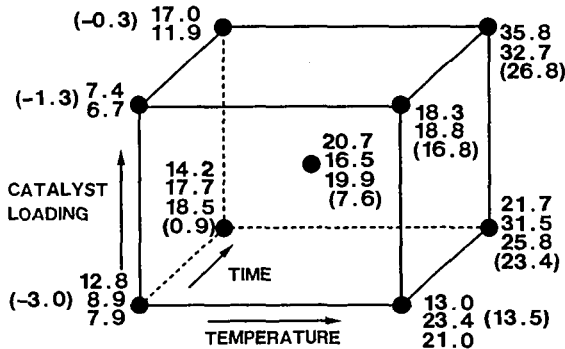
(TEMPERATURE = °C; TIME = MINUTES; CATALYST LOADING = WT % AR COAL)

FIGURE 2.
MEASURED THF CONVERSIONS
(PNL'S 6-LINE FERRIHYDRITE + WYODAK COAL)



PARENTHESES = AVERAGE MEASURED VALUES FROM BLIND CANYON COAL

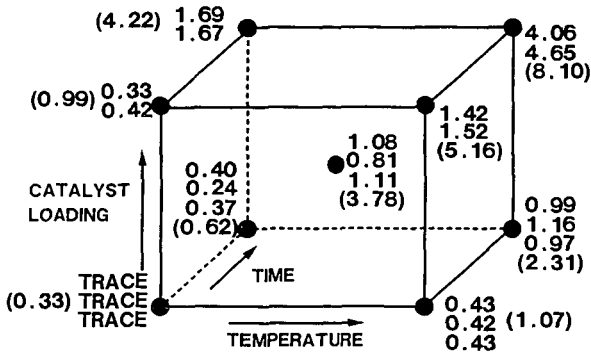
FIGURE 3.
MEASURED HEPTANE CONVERSIONS
(PNL'S 6-LINE FERRIHYDRITE + WYODAK COAL)



PARENTHESES = AVERAGE MEASURED VALUES FROM BLIND CANYON COAL

FIGURE 4.

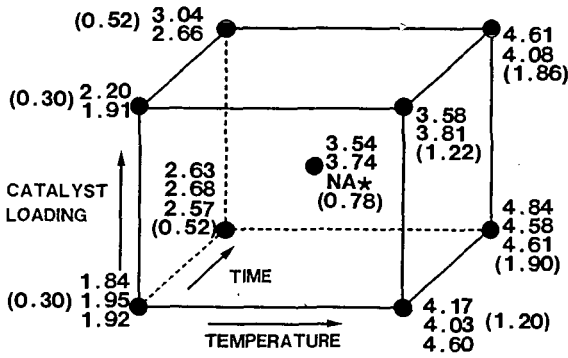
DHP (%) IN REACTION PRODUCT
(PNL'S 6-LINE FERRIHYDRITE + WYODAK COAL)



PARENTHESES = AVERAGE MEASURED VALUES FROM BLIND CANYON COAL

FIGURE 5.

GAS YIELD (%dmnf)
(PNL'S 6-LINE FERRIHYDRITE + WYODAK COAL)



PARENTHESES = AVERAGE MEASURED VALUES FROM BLIND CANYON COAL
* NOT AVAILABLE